

# **FINAL REPORT**

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**THE SPECTROSCOPIC, CHEMICAL AND PHOTOPHYSICAL PROPERTIES OF MARTIAN SOILS AND THEIR ANALOGS (MERC-PHASE II)**

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## ABSTRACT

A series of variably proportioned iron/calcium smectite clays and iron loaded smectite clays containing iron up to the level found in the martian soil have been prepared from a typical montmorillonite clay using the Banin method (Banin, 1973). Evidence has been obtained which supports the premise that these materials provide a unique and appropriate model soil system for the martian surface in that they are consistent with the constraints imposed by the Viking surface elemental analyses, the reflectance data obtained by various spacecraft instruments and ground-based telescopes, and the chemical reactivity measured by one of the Viking 'biology' experiments, the Labeled Release (LR) experiment.

## RESULTS AND DISCUSSION

### A. PREPARATION OF MARS SOIL ANALOG MATERIALS (MarSAM)

The preparation of several sets of MarSAM by the Banin (1973) ion-exchange process has been done. These sets were:

- 1985 - A suite of five variably ion-exchanged iron/calcium SWy-1 montmorillonite clays with 0, 20, 50, 80 and 100% adsorbed iron, and an Otay montmorillonite clay with 100% adsorbed iron. This suite was used to establish spectral and chemical analogy of iron-exchanged clays to the martian soil and to develop the protocols for reflectance and quantitative NIR analysis of MarSAM samples.
- 1986 - A suite of eight SWy-1 montmorillonite clays containing adsorbed/precipitated iron to 250% of the cation exchange capacity (CEC) (total content of  $\text{Fe}_2\text{O}_3$  of up to 9-10% by weight of the clay). This suite serves as a better elemental analog to Mars soil with respect to iron content, and was characterized with respect to its total elemental composition and surface-ion composition.
- 1987 - Large quantities of four modified SWy-1 montmorillonite clays, containing 0, 50 and 100% of CEC as adsorbed iron (with calcium as the complementary ion), and 100% adsorbed  $\text{H}^+(\text{Al})$ , for the study of radiation and environmental effects on the spectral properties of Fe/Ca MarSAM (See L. M. Coyne report).
- 1988 - A series of modified SWy-1 montmorillonite clays containing up to ~19%  $\text{Fe}_2\text{O}_3$  (about 600% of CEC). These clays served to elucidate the role of amorphous iron, either chemically adsorbed or co-precipitated on the clay surface, in concentrations similar to those found in Mars soil, on the chemical and spectral properties of the MarSAM.

## **B. CHARACTERIZATION OF MarSAM**

### **1. Elemental Analysis**

The elemental composition (as oxides of major (Si, Al, Ti, Fe, Mn, Mg, Ca, Na, K and P) and trace (Rb, Y, Sr, Cs, Br, Zr and Zn) elements) of the 1985 MarSAM were determined. The major elements were determined quantitatively using a wavelength dispersive X-ray fluorescence (XRF) spectrometer, while the trace elements were analyzed in a semiquantitative fashion with an energy dispersive XRF instrument. Because of the limited amounts of samples available, a micro-technique was adopted for the analysis of the major elements. Inductively coupled plasma (ICP) was used to check the results of the XRF procedures for the following elements: Si, Al, Fe, Mg, Ca, Ti and Mn. The results of the elemental analyses showed that the ion-exchange procedure used for preparing the modified clays removes most of the Na, Ca, and P, and some of the K and Mg. This is expected as these elements are present as adsorbed ions, in soluble salts or in minor accessory minerals. The major matrix elements Si and Al remained essentially unchanged. A more detailed discussion of the results is given in a published paper. (Banin et al., 1988, Appendix A). A complete elemental match between MarSAM-1985 samples and Mars soil, as understood from existing data, was not attempted at the present time as this MarSAM suite was synthesized to study the chemistry and spectroscopy of adsorbed iron in the clay matrix and to establish the chemical analogy of iron-exchanged clays to Martian soil. An important conclusion that follows from the elemental analysis of the major elements of the MarSAM-1985 is that the Banin ion-exchange procedure used to prepare the clays does not affect the crystal lattice to a discernible extent, as evidenced by the constancy of results for the major elements silicon, aluminum, titanium and manganese.

### **2. Surface Ion Composition and Physico-Chemical Characteristics**

Detailed characterization of the surface-ion composition, redox potentials and particle size distributions by SEM measurements were done for the 1985 and 1986 series of MarSAM. The data for the 1985 suite are discussed in detail in Banin, et al. (1988). Generally, the clay modification procedure that was used (Banin, 1973) has repeatedly produced clays of controlled composition, and has given reproducible, stable and self-consistent results in the many tests to which they were exposed over

the last few years, including the LR simulation, light reflectance in the UV-VIS-NIR wavelength range, thermoluminescence and ESR (Banin and Rishpon, 1979; Banin et al., 1985; Coyne and Banin, 1986; Banin et al., 1988).

The smectite structure was essentially not damaged or changed by the procedure in which the clay was loaded with adsorbed iron up to ~14% Fe<sub>2</sub>O<sub>3</sub>, bringing it (together with the structural iron) to a total iron content of 17-19% Fe<sub>2</sub>O<sub>3</sub>, as found in the Mars soil. This is shown by the recently obtained X-ray diffraction spectra of the crude and treated clays (Figure 1). Note that the montmorillonite peaks are dominant in both the crude and treated clays and that no diffraction peaks for crystallized iron minerals appear, except at the highest level of iron addition.

The X-ray diffraction spectra of the iron-clays supply direct evidence of the non-crystallinity of the iron oxides, by showing only a few weak peaks characteristic of crystalline iron oxides, that may be tentatively assigned to goethite ( $\alpha$ -FeOOH), appearing in the clay-iron oxide preparation with the highest level of added iron (Figure 1).

The reflectance spectra of the Fe loaded clays in the UV-VIS-NIR range maintain the similarity to the Mars bright-region spectra (Banin et al., 1985; Banin et al., 1988, Appendix A) in that, even at high iron loads, the typical d-d iron absorption bands in the 0.4-0.9  $\mu$ m wavelength range are not distinguishable. Comparison of these spectra with those reported for physical mixtures of clays with well crystallized iron oxides (Singer, 1982), shows that at comparable iron-oxide contents, clear and well recognized absorption features can be seen in the physical mixtures. This indicates that crystallization of iron adsorbed/precipitated on the clay by our procedure was inhibited. These findings reinforce our hypothesis that amorphous iron oxides in a clay system, modified by our procedure, may be an appropriate analog for the silicate phases and the iron phases in the martian soil.

### 3. Micromorphological description of the precipitated iron-phases

Transmission electron microscopy (Photo 1, Ben-Shlomo and Banin, unpublished data) showed no discrete particles of iron oxides forming until added iron reached 3-4% Fe<sub>2</sub>O<sub>3</sub> but the clay particles became more electron-dense indicating fine coating with the added iron. Small, electron-dense discrete isodiametrical particles appeared at added iron contents above 8-9% Fe<sub>2</sub>O<sub>3</sub>. Needle-shaped particles were observed in the preparation with the highest iron content. However, the iron oxide-oxyhydroxy particles were in a size range smaller

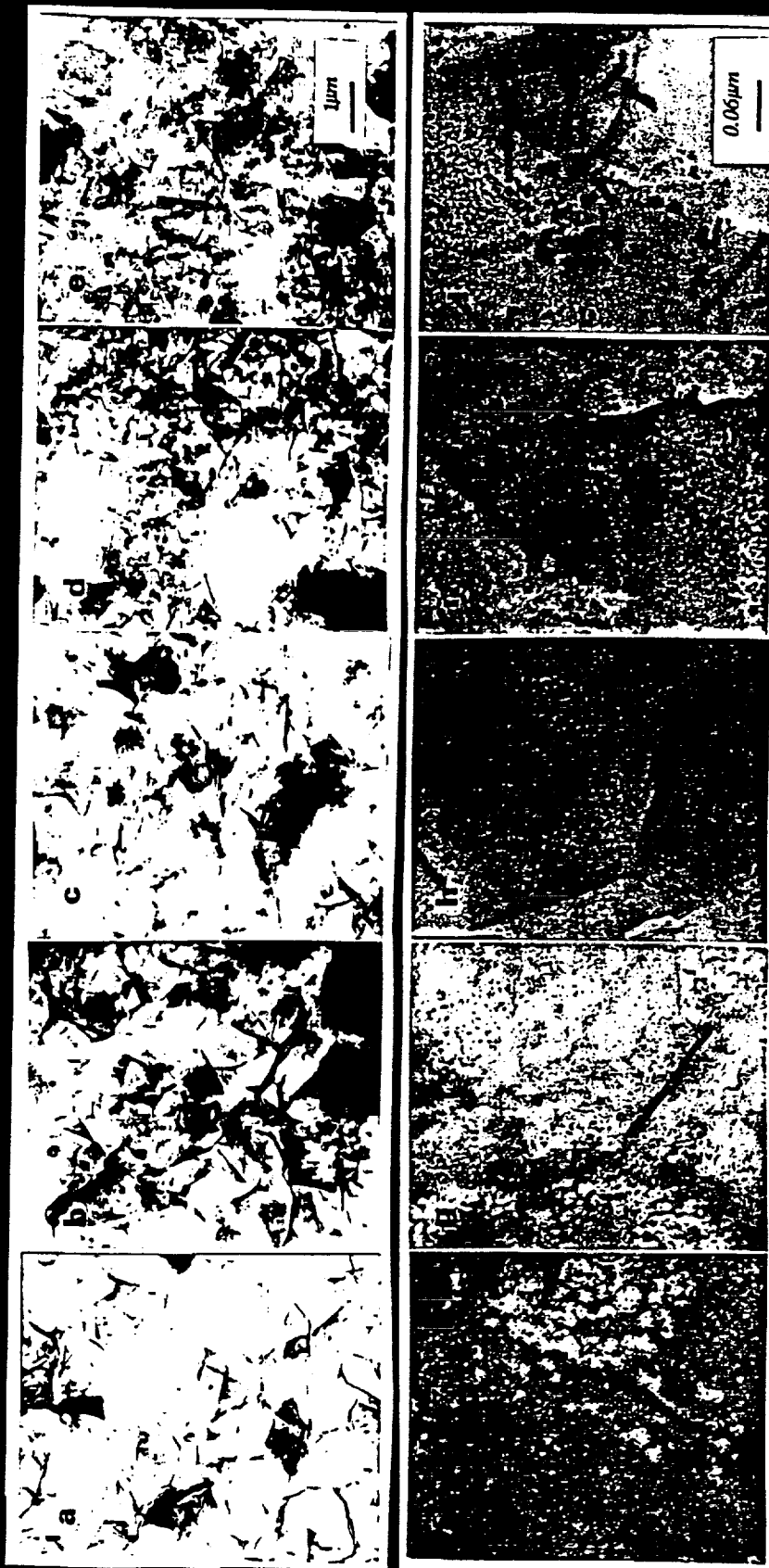


Photo 1: Transmission electron micrographs of montmorillonite enriched with iron oxide-oxyhydroxide (MoFeOx).

Added iron (as %Fe<sub>2</sub>O<sub>3</sub>) in the various preparations is 0, 4.13, 6.75, 9.61 and 15.8 in (a) - (e), respectively (magnification x10,000) and (f) - (j) respectively (magnification x160,000).

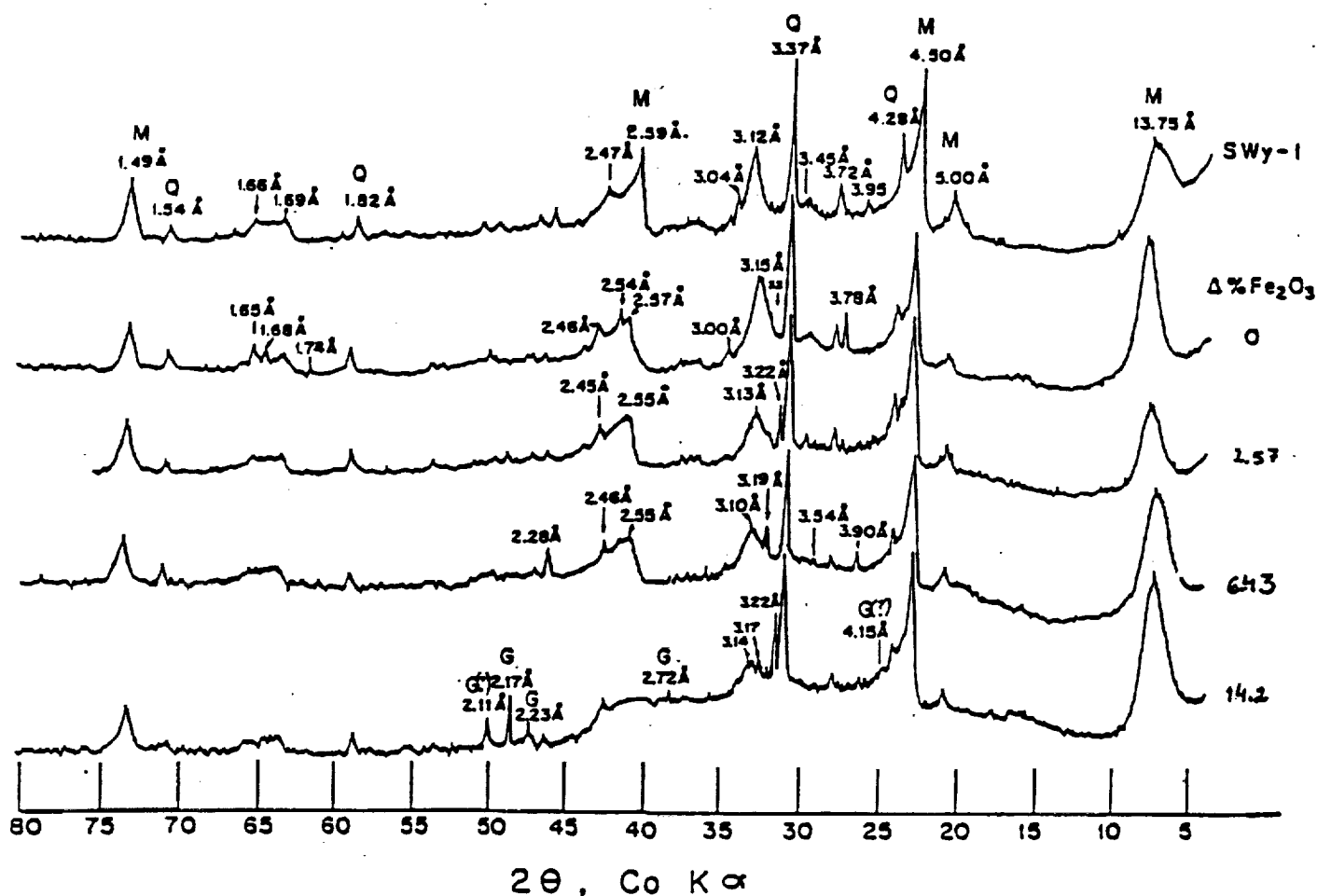


Figure 1: X-ray diffractograms of MarSAM with different nominal loadings of iron-oxyhydroxide. They were obtained for non-oriented powders on (from top to bottom): the crude clay (SWy-1), the modified, acid-leached clay with no adsorbed iron (0), and clays with 2.57%, 6.43% and 14.2% added  $\text{Fe}_2\text{O}_3$ . The labeled peaks are: M=montmorillonite, Q=quartz, and G=goethite(?).



than reported in the literature for hematite and goethite (3-5 nm vs. 100-500 nm and 70-100 vs. 200-800 nm, for the isodiametrical and needle-shaped particles, respectively).

It appears that the presence of soluble Al and Si released from the clay and perhaps the large specific surface area of the smectite, played a major role in the inhibition or retardation of crystal growth of the iron phases. Even at iron oxide concentration of up to 15%  $\text{Fe}_2\text{O}_3$ , the smectite clay acted as a "retarding matrix" preventing through chemical effects and/or steric hindrances, the crystal-growth of iron oxyhydroxide deposited onto it. Such effects may explain the apparently limited crystal growth of iron-oxides in the martian soil.

#### 4. Water adsorption isotherms

Water adsorption by clays with variable amounts of adsorbed iron/calcium, specifically 0, 50 and 100% adsorbed Fe, depicted a complex dependence on the exchangeable ion composition and on the relative humidity. The water adsorption isotherm for the Ca-clay was similar to those reported before in the literature. As for the Fe-clay, to the best of our knowledge, no detailed adsorption study has been reported yet for such a clay. A detailed discussion of the findings is presented in Banin et al. (1988) (Appendix A). The general shape of the adsorption isotherms and the differences between the various ionic forms could be explained on the basis of a model describing water interaction with clay surfaces (Sposito and Prost, 1982). A sequence of stable molecular configurations for water has been proposed to describe the adsorption process. On the basis of this we predicted that the adsorption isotherms and, thus, those catalytic and spectral properties of the clay associated with moisture content will be most sensitive to the ionic composition at moisture contents between 4 and 8  $\text{H}_2\text{O}$  molecules per unit cell (10-20% adsorbed moisture) at which level the solvation envelopes around the cations are being formed.

Since the surface-chemical reactivity of clays is strongly affected and modulated by the state and amount of adsorbed water, it is expected that Martian soil reactivity (if smectite clays are major components) will be (a) modulated by the amount of adsorbed water, (b) more strongly fluctuating at certain moisture contents than at others depending on the stability of the water molecular configuration, and (c) temporally and spatially variable in relation to soil composition as well as to atmospheric variations at the planet's surface.

### C. REFLECTANCE SPECTROSCOPY

SWy-1 montmorillonite, a smectite clay, from Crook County, Wyoming was used as the starting material for the preparation of a Mars soil analog. This parent clay was obtained from the Clay Mineral Society Repository at the University of Missouri, Columbia, Missouri, and was in powder form. Using the "Quantitative Ion Exchange Method" of Banin (Banin 1973; Banin et al., 1988), the crude clay was converted to a form containing  $15.8 \pm 0.4$  wt % Fe as  $\text{Fe}_2\text{O}_3$  as determined by wavelength dispersive X-Ray fluorescence (XRF). This is equivalent to approximately 600% of the iron necessary to fill all of the cation exchange sites available in the clay. The fraction of iron beyond 100% of the exchange capacity is thought to be adsorbed onto the surface of the clay as oxyhydroxy iron colloids at the nanocrystalline level (Banin, 1989). The palagonite is a sample of basaltic glass collected at several locations on the upper slopes of Mauna Kea on the island of Hawaii. This palagonite contained  $11.1 \pm 0.5$  wt % Fe as  $\text{Fe}_2\text{O}_3$ . XRF elemental analyses of palagonite, the clay samples, and the Mars surface from Viking are shown in Table I. For XRF analysis, fused glass disks were prepared using 800 mg of sample mixed with 8.000 g of lithium tetraborate flux using the Wahlberg-Taggart method (Taggart et al., 1987). The XRF analysis was carried out using an ARL model XRD-8600B wavelength dispersive spectrometer.

Mixtures of palagonite and iron montmorillonite were prepared on a wt % basis. The pure materials and the mixtures were ground and mixed for one minute on a Wig-L-Bug before their spectra were measured. An estimate of the particle size of the palagonite and iron montmorillonite was done using a light microscope. In both samples, the vast majority of aggregate particles

Table I. Average elemental composition of Mars surface fines, palagonite and iron-rich montmorillonite clay from XRF.

-----% by wt-----			
<u>elemental oxide</u>	<u>Mars<sup>1</sup></u>	<u>Montmorillonite<sup>2</sup></u>	<u>Palagonite<sup>2</sup></u>
SiO <sub>2</sub>	43	53.0	38.8
Al <sub>2</sub> O <sub>3</sub>	7	16.8	19.0
Fe <sub>2</sub> O <sub>3</sub>	17.6	15.8	14.8
MgO	6	2.1	4.60
CaO	6	.38	5.36
TiO <sub>2</sub>	0.65	0.11	3.30
Cl	0.7	--	--
SO <sub>3</sub>	7	--	--
MnO	--	<.02	0.25
K <sub>2</sub> O	--	0.31	0.58
Na <sub>2</sub> O	--	0.30	2.60
P <sub>2</sub> O <sub>5</sub>	--	<.02	0.85
LOI	--	12.90	11.60

(1) Banin, Clark, and Wanke, 1989; (2) USGS, Menlo Park;

were estimated to be in the 1-5  $\mu\text{m}$  size range, with a minority portion of each having some sub-micron particles as well as some particles in the 25-50  $\mu\text{m}$  range. Since particle size distribution was estimated to be about the same using light microscopy, this parameter is not expected to be a variable of concern in the recorded spectra of the mixtures. Samples of approximately 1.2 g were pressed into stainless steel planchettes sample holders 25.4 mm in diameter and 2.5 mm deep using an ECC (English China Clays, Ltd., London) press. This press provided a pressure of 1.2 kg  $\text{cm}^{-2}$  on the sample, resulting in a compact, but softly packed pellet. A 20 second pressing time was used for all of the samples. This method of pressing is a standard method of sample preparation employed for reflectance measurements of clay samples (English China Clays, Intl., Test Method P110). Using a standardized pressing technique obviated the need to account for particle packing as a variable in reflectance spectra for this study which was designed to investigate the effects of mixture composition and surface substitution. Mars may not be expected to be compacted to the same level. The samples were stored in a desiccator before mixing, after mixing, and until their spectra were recorded. All had the same amount of exposure to ambient air. No further efforts were attempted in these experiments to control the relative humidity, and thus, the amount of adsorbed water.

Reflectance spectra from 0.3 to 2.5  $\mu\text{m}$  were recorded on a Perkin Elmer Lambda 9 spectrophotometer (Norwalk, CT) using a Labsphere DRTA-9A Diffuse Reflectance and Transmittance Accessory (North Sutton, NH). Reflectance data presented below thus represent hemispherical reflectance. The spectral bandpass was set between 1/5 and 1/10 of the widths at half height of the spectral features of interest by setting the slits to 2.0 nm in the UV/VIS. This allowed for a constant spectral resolution ( $\pm 10\%$ ) in the

UV/VIS. In the NIR , an automatic slit program was used to maintain a constant energy level during spectral scanning (120 nm/min). Halon was used as reference material in both beams of the spectrophotometer for instrument background correction and as the standard reflectance material in the reference beam during sample recording. In order to prevent the lightly packed sample from falling into the reflectance sphere from its vertical sample position, a fused quartz plate (Precision Cells Inc., Hiskville, NY) contained in a custom fabricated sample holder was used in the sample beam only. The fused quartz plate was also placed in front of the halon during background correction. All spectra were digitized using Perkin Elmer CUV-3 software installed on a Perkin Elmer model 7700 data station. CUV-3 software operates the lambda 9 spectrophotometer, and collects and processes the spectral data. The Savitzky/Golay smoothing function, which determines the best fit of a quadratic polynomial through successive data windows, was used to smooth the spectra. Twenty five point data windows were used in the smoothing.

Figure 2 shows a composite reflectance spectrum of typical high albedo regions of Mars taken from telescopic observations from Earth (Singer et al., 1979). The ordinate is relative reflectance scaled to a value of 1.0 at 1.02  $\mu\text{m}$ . From the UV to 0.75  $\mu\text{m}$ , the spectrum is almost featureless except for an increase in reflectance and subtle slope changes at 0.5 and 0.6  $\mu\text{m}$ . A shallow absorption band is seen with its central position at 0.87  $\mu\text{m}$ . These features have all been attributed to  $\text{Fe}^{3+}$  (Singer, 1982; Sherman, et al., 1982), either as  $\text{Fe}^{3+}\text{-O}^{2-}$  charge transfer absorptions or  $\text{Fe}^{3+}$  crystal field transitions. Weak, narrow bands at 1.45 and 1.62  $\mu\text{m}$  and a stronger composite band in the 1.9 to 2.1  $\mu\text{m}$  region seen in the martian spectrum are attributed to  $\text{CO}_2$  in the martian atmosphere. A broad, shallow band observed

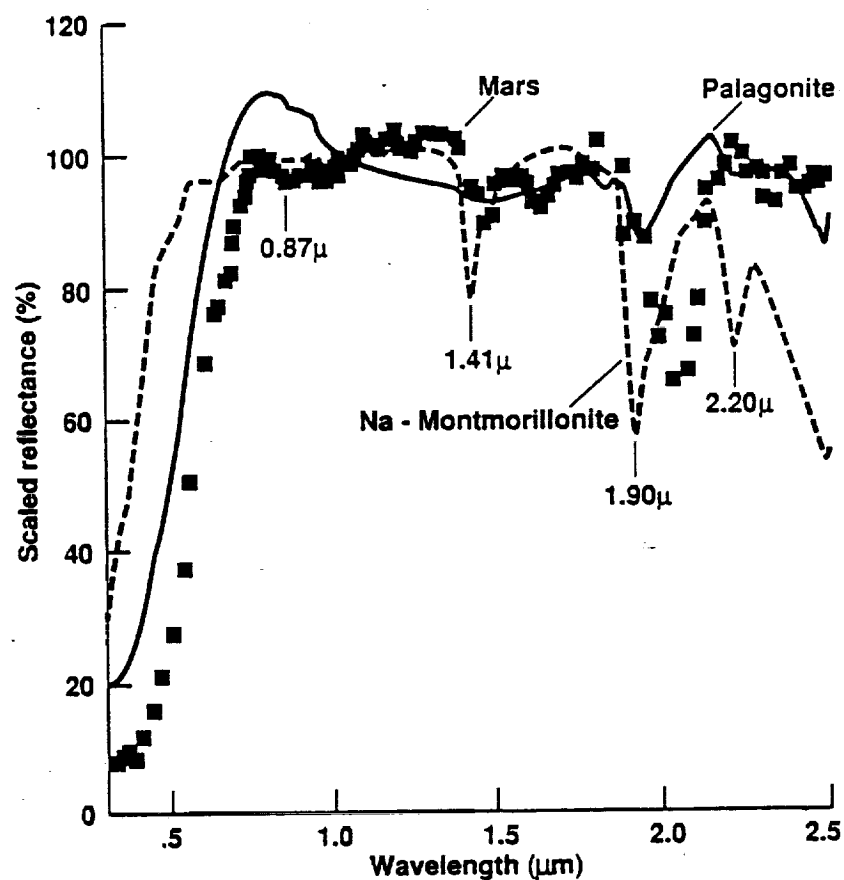


Fig.2 Diffuse reflectance spectra of palagonite and Na-montmorillonite and representative composite reflectance spectrum for Martian bright regions. All spectra are scaled to unity at 1.02  $\mu\text{m}$ . The bright region of the Martian spectrum is an average of the brightest areas observed in 1973 (McCord et al., 1977), while the near-infrared is an average of the brightest areas observed in 1978 (McCord et al., 1982).

in the region between 1.4 and 1.7  $\mu\text{m}$  which is superimposed on the sharper  $\text{CO}_2$  band has been interpreted as being due to water ice in or on the surface of Mars (McCord et al., 1982). Beyond 2.1  $\mu\text{m}$ , the martian spectrum is relatively flat with some hint of fine structure around 2.3-2.4  $\mu\text{m}$ . Recently obtained higher spectral resolution data from the 1988 opposition in the 2.0 - 2.5  $\mu\text{m}$  region have resolved the absorption envelope of the 2.36  $\mu\text{m}$  band into 5 distinct and relatively sharp bands. These have been interpreted by Clark et al. (1990) as being due to the mineral scapolite, but an alternative interpretation suggests that atmospheric CO as well as a solid phase contribute significantly to this 2.36  $\mu\text{m}$  band envelope (Roush and Pollack, 1989; Roush, Blaney and Singer, 1990).

A comparison of the scaled reflectance spectra of palagonite and Na-montmorillonite, the natural cation form of Wyoming bentonite, to the martian spectrum (Singer et al., 1979) region is also shown in Figure 2. Montmorillonite with its natural terrestrial cation was chosen for this comparison to facilitate showing which spectral features can be assigned to the clay structure itself and differentiated from those features attributable to exchanged and adsorbed iron. To facilitate comparison to the telescopic data which was scaled to a reflectance of 1.0 at 1.02  $\mu\text{m}$ , the spectra of the two minerals was scaled similarly. In the region from 0.30 - .70  $\mu\text{m}$ , the spectra are without marked features; all spectra show a drop-off into the ultraviolet. The clay spectrum has a unique slope change occurring around 0.35  $\mu\text{m}$  attributable to  $\text{Fe-O}^{2-}$  and other charge transfer bands or crystal field absorptions of iron (Karickhoff and Bailey, 1973; Chen et al., 1979; Banin et al., 1985). At about 0.5  $\mu\text{m}$ , a slope change is noticeable in all three spectra. A band at .62  $\mu\text{m}$  in the clay spectrum is not observed in the other spectra. The Mars spectrum exhibits a moderately intense band at .87

$\mu\text{m}$  which is weak in the spectrum of palagonite and very weak in the clay spectrum. This band has been assigned to  $\text{Fe}^{3+}$  by Huguenin et al. (1977).

From 1.3 - 2.5  $\mu\text{m}$  (Fig.2), there are some marked differences between the analog mineral spectra and the Mars spectrum. Two relatively intense absorption bands at 1.4 and 1.9  $\mu\text{m}$  are observed in both palagonite and Na-montmorillonite; in palagonite, these bands are both broader and weaker than in the clay, especially at 1.4  $\mu\text{m}$ . The band at 1.4  $\mu\text{m}$  has been suggested as being due to both adsorbed water and structural hydroxyls (OH stretch overtones); the band at 1.9  $\mu\text{m}$  has been attributed solely to adsorbed water (H-O-H bend overtones) (Hunt and Salisbury, 1970; Hunt 1977). As can be seen from the martian spectrum,  $\text{CO}_2$  in the martian atmosphere causes some interference with the 1.4 and 1.9  $\mu\text{m}$  bands. An intense band at 2.2  $\mu\text{m}$  in the spectrum of Na-montmorillonite and a small, but noticeable inflection in the spectrum of palagonite at the same wavelength (since palagonite by definition is a mixture of minerals, "contamination" of the palagonite with clay or other minerals is likely) are attributable to clay lattice hydroxyls from combinations of the O-H stretch and cation (Al) O-H bend or lattice modes (Hunt, 1977; Hunt and Salisbury, 1970). In dioctahedral clays like montmorillonite, the cation is generally  $\text{Al}^{3+}$ . This 2.2  $\mu\text{m}$  band is diagnostic of mineralogy and is interpreted as being indicative of aluminous hydroxylated minerals such as montmorillonite or kaolinite. As previously suggested (Singer, 1985; Roush et al., 1990), the absence of the 2.2  $\mu\text{m}$  band in the spectrum of Mars indicates that well crystalline, aluminous hydroxylated materials such as dioctahedral montmorillonite cannot be present on the surface of Mars as a major mineral. It does not exclude montmorillonite from being present as a minor and, perhaps significant mineral on the surface.



A final point of comparison in Figure 2 occurs in the spectral region from 2.2 to 2.5  $\mu\text{m}$ . The clay spectrum shows a drop-off in reflectivity which is less obvious in the palagonite spectrum and not observed in the Mars spectrum. Since the drop-off has been attributed as arising from the 3  $\mu\text{m}$  fundamentals of water, this has been interpreted to indicate that the Mars soil is more desiccated than either the montmorillonite or palagonite analogs (Bruckenthal, 1987; Roush, Blaney, and Singer, 1989).

A similar comparison to that of Figure 2 is shown in Figure 3 except that an iron rich ( $15.8 \pm 4$  wt % Fe as  $\text{Fe}_2\text{O}_3$ ) Mars analog montmorillonite has been substituted for Na-montmorillonite. The spectral analysis is similar to that of Figure 1. In the 0.30 to 0.70  $\mu\text{m}$  region, Fe-montmorillonite shows qualitatively a closer correspondence to the steep increase in slope of reflectance associated with the Mars spectrum than does palagonite. This agrees with the high spectral resolution data recently presented by Bell et al. (1989) where the investigators concluded that the bands and slope of the Mars spectrum in this wavelength region are indicative of crystalline iron oxide minerals which are suggested to be present in the martian surface soil. As mentioned above, Banin (1989) has proposed that iron-rich clays containing iron above the cation exchange capacity contain the excess iron as adsorbed nanocrystalline iron oxide. This would explain the closer correspondence of the Fe-clay spectrum to that of Mars in the 0.30-0.70  $\mu\text{m}$  spectral region compared to the spectrum of Na-clay. The prominent 2.2  $\mu\text{m}$  band is still quite obvious in the spectrum of this iron-enriched montmorillonite clay which is inconsistent with the Mars spectrum. The maintenance of the shape and depth of the 2.2  $\mu\text{m}$  band in the iron-rich clay implies that the clay lattice structure is probably unaffected by the iron substitution process.

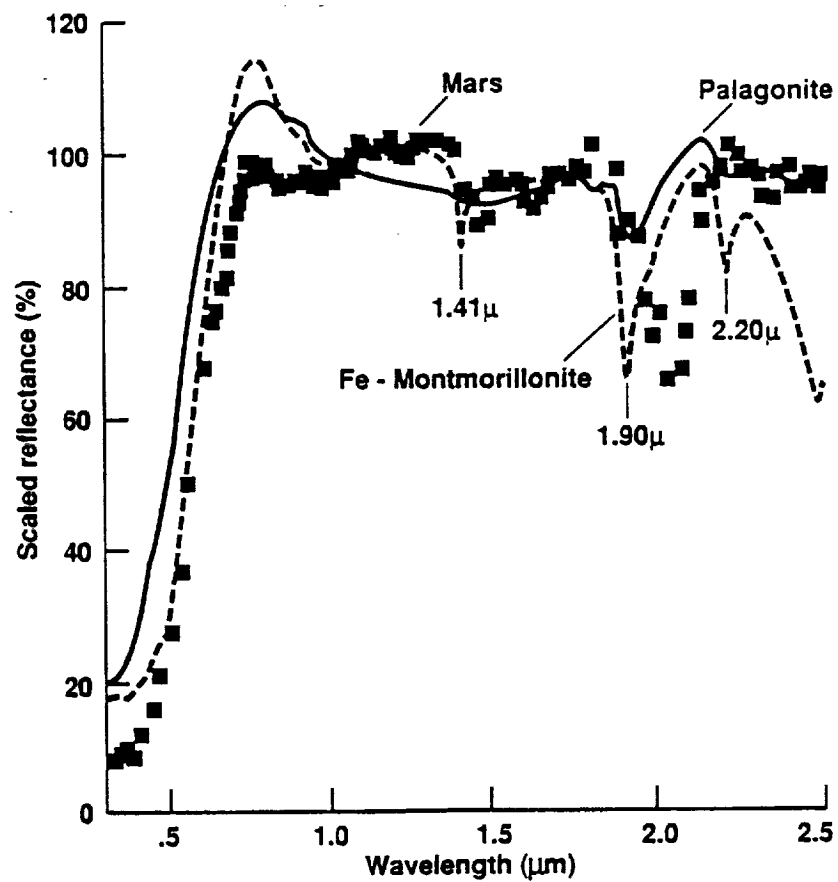


Fig. 3 A comparison of the diffuse reflectance spectra of palagonite and Fe-montmorillonite ( $15.8 \pm 0.4$  wt % Fe as  $\text{Fe}_2\text{O}_3$ ) with the Mars reflectance spectrum of Fig. 1. All spectra are scaled to unity at  $1.02 \mu\text{m}$ .

At the writing of this report, it was concluded by visual evaluation that in mixtures of palagonite and montmorillonite clay, up to 30% by weight of clay (70% by weight palagonite) can exist without being detected spectroscopically (Fig.3). It must be expected that the mineralogy of Mars will be complex. The Mars lithosphere, like Earth's, has been and still is interacting with the atmosphere, and this is likely to produce secondary minerals as weathering or alteration products as a mixture of minerals composing the soil.

#### **D. SIMULATION OF THE VIKING LABELED RELEASE EXPERIMENTS WITH MarSAM**

Experiments were conducted with three clays (0, 50 and 100% Fe) each at two water contents. The results are reproduced in Figure 4. They show again the appropriateness of using clays, saturated with iron, as MarSAM. These clays successfully simulate the chemical-catalytic processes observed during the Viking mission when a solution of several simple organic compounds was added to the Martian soil and the decomposition of one of those compounds (believed to be the formate) was observed. Furthermore, the present results showed that adsorbed water on the clay surface reduced the decomposition activity in the LR reaction so that it agreed less favorably with the results obtained on Mars. This narrows further the range that may be predicted for water contents in the Martian soil. A detailed discussion of these data is given in Banin et al (1988), (Appendix A).

Palagonite, an alteration product of basaltic glass, has been proposed on the basis of spectral conformity to Mars reflectance in the visible range, as a sole and completely satisfactory Mars soil analog. We have used the LR simulation method to test whether palagonites satisfy another constrain for the mineral nature of the Mars soil, i.e., its demonstrated chemical reactivity and its ability to decompose certain organic compounds.

Palagonites representing a wide range of formation conditions on Earth failed to show such reactivity whereas iron clay does (Figure 5). The pH of these palagonites in water slurries was found to be in the range of 7.0-9.0, possibly due to buffering by Ca or Mg carbonates and/or silicic acid released from the palagonite or from the basalt glass. Even extensive acid leaching of the palagonites did not result in increased reactivity in the LR simulation experiments. The few palagonites showing some reactivity (much lower than that measured on Mars) had higher specific surface areas and were more extensively weathered, possibly containing higher proportions of weathered smectite minerals. Basaltic glass weathering on Mars, advancing along a somewhat unique pathway, different from palagonitization on Earth, may have resulted in a more highly crystalized smectite-phylosilicates while maintaining the iron oxide-oxyhydroxides as amorphous coatings or as nano-phases.

The simulation results show that palagonites do not fully comply with the chemical-reactivity criteria and constraints for Mars soil mineralogy. Further study is required to resolve the apparently conflicting results of the spectral observations and the chemical simulations, regarding the mineralogy of the Mars soil.

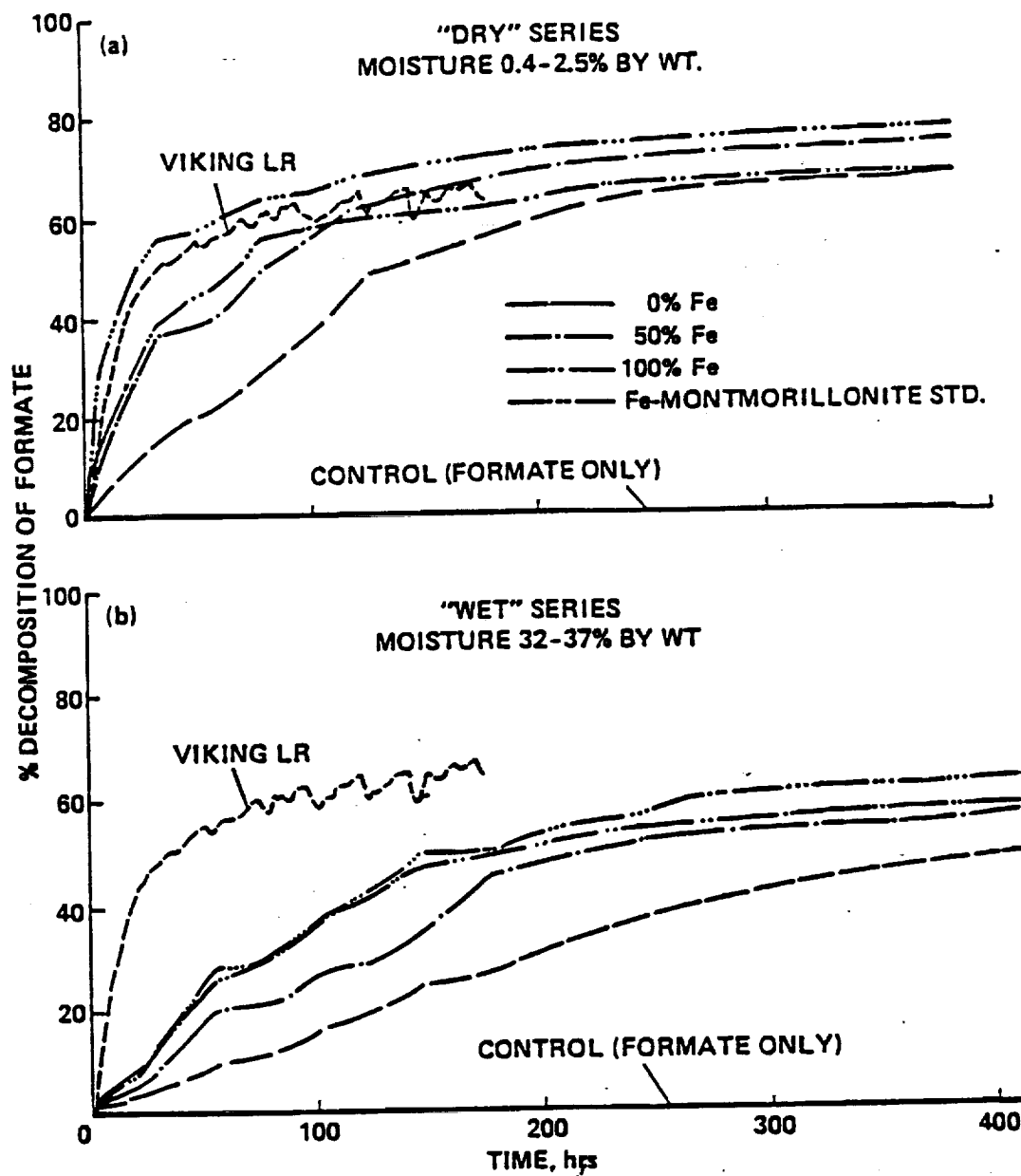


Figure 4: Decomposition of sodium formate by four iron-calcium montmorillonite clays at two moisture contents and by the martian soil in the Viking Labeled Release experiment.

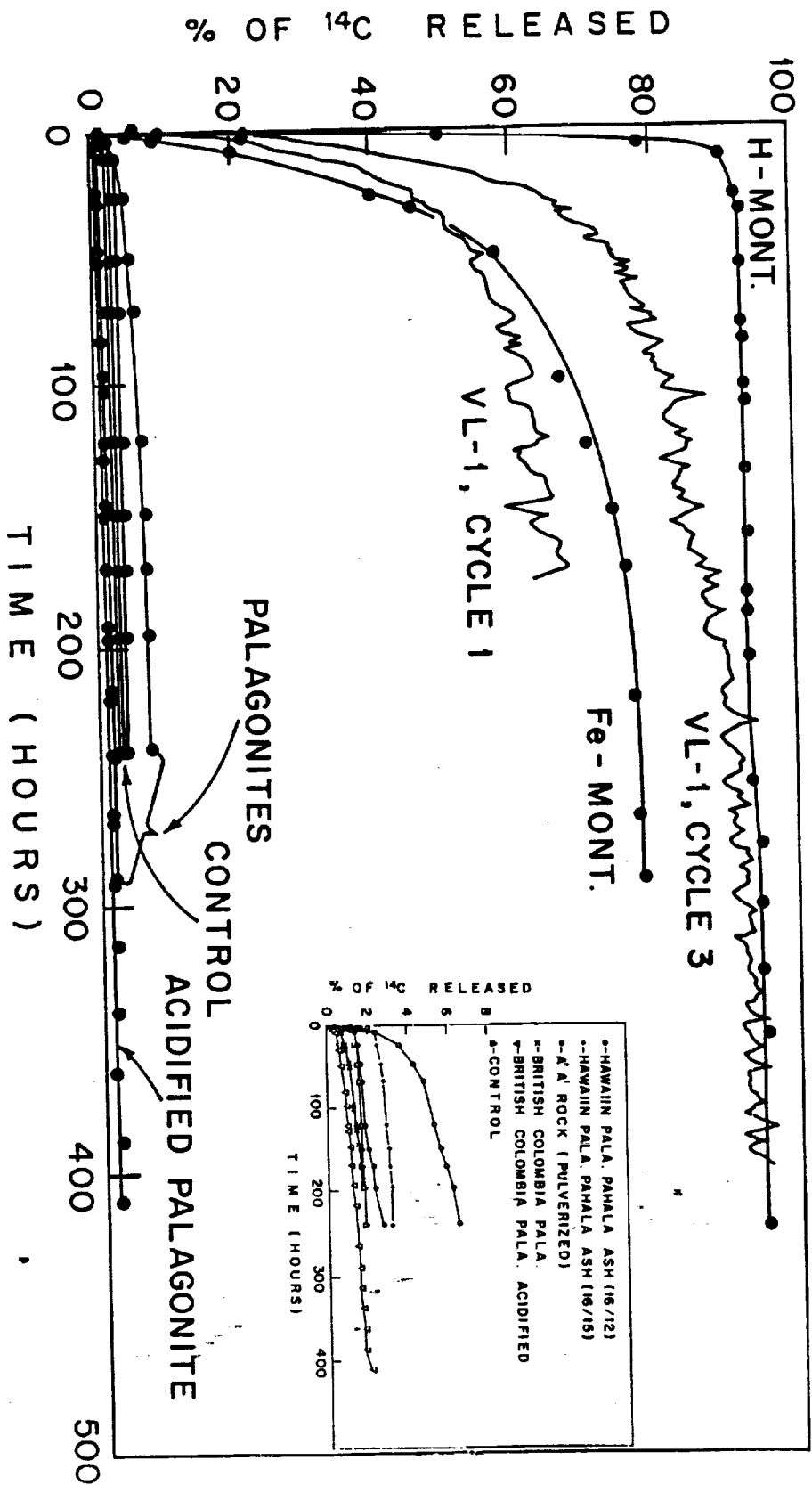


Figure 5: Kinetics of  $^{14}\text{C}$  release caused by Mars soil in two cycles of the Viking Labeled Release Experiment (VL-1), compared with simulations using iron and hydrogen montmorillonite (H- and Fe-Mont), and various palagonites.

## SUMMARY

Among the numerous candidates proposed since 1976 as Mars soil analogs, smectite montmorillonite clays containing adsorbed iron appear to satisfy the largest number of qualitative constraints known at present. The presence of clays on Mars may strongly affect its climatological cycles, land forming and shaping processes, and volatile cycles. Furthermore, establishing the presence of clays as a major and active component of the Martian soil and dust will be a clue to an evolutionary step on Mars when liquid water was present. Potentially the presence of significant amounts of water may have made possible primitive abiotic or biotic evolution, whose organic remnants may still be found in buried sediments. To these ends, we have carried out a number of experiments studying various properties of a suite of iron-calcium and iron enriched montmorillonite clays as a model for the Martian soil. In summary, we have:

1. Prepared a monomineralic model for Mars aeolian material in which:
  - a) the parent material is a natural montmorillonite clay and
  - b) several properties, including surface iron and precipitated iron can be systematically varied.
2. Measured the reflectance spectra of the above clays from 2-25  $\mu\text{m}$  and found:
  - a) two absorption features at (.5-.6 and .95  $\mu\text{m}$ ) whose intensity increases with increasing surface iron,
  - b) satisfying qualitative agreement between the spectra of our clays and of Mars (in the VIS-NIR range), and
  - c) that the correspondence between the MarSAM and Martian surface spectra improved as the iron contents of the MarSAM were made increasingly similar to that found in the martian soil.
3. Measured water adsorption isotherms (at 22°C) of the MarSAM and found them to:
  - a) be generally characteristic of multilayer adsorption processes,
  - b) show cation-dependent hysteresis, i.e., to be dependent on surface coverage of both water and exchangeable cations,

- c) show three regions corresponding of  $\leq 1$  adsorbed monolayer of water (at 20% R.H.), 1-2 monolayers (20-70% R.H.), and  $\geq 2$  monolayers (>70% R.H.)
- d) exhibit maximum sensitivity to the cation type in the range of 20-70% relative humidity, as would be expected for sequential hydration and

We predict that for the anticipated humidity of Mars the dependence of the isotherms on cation type would be minimal, as the water is strongly bonded to the silicate layer as well as to the cations.

4. Measured the rate of decomposition of sodium formate, as evidenced by the release of labeled  $\text{CO}_2$ , by the clays, as function of iron content and relative humidity in simulations of the Viking LR experiment and found that:

- a) the rate of decomposition increased with increasing iron content and with decreasing water content,
- b) the decomposition reaction kinetics was similar to that found with the martian soil as observed by the Viking Landers, and,
- c) no decomposition reaction was caused by palagonites, which thus do not fully comply with the known constraints for Mars-soil composition and reactivity.

5. Measured the reflectance spectra (.3 -2.5  $\mu\text{m}$ ) of two likely, Mars, analog minerals, palagonite and iron-rich montmorillonite clay, and showed that:

- a) up to 30 wt % of iron-rich montmorillonite clay (containing  $15.8 \pm 0.4$  wt % Fe as  $\text{Fe}_2\text{O}_3$ ) may be present with palagonite on the surface of Mars and the remotely sensed reflectance spectrum of Mars may not reveal this.



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## **Appendix**

## Appendix B: Publications and Presentations

### Refereed Publications

1. Banin, A., 1986. "Clays on Mars" (An invited review, contributed to the book "Clays and the Origin of Life", edited by H. Hartman and A.G. Cairns-Smith), Cambridge University Press. pp. 106-115.
2. Coyne, L.M., and Banin, A., 1986. Effect of adsorbed iron on thermoluminescence and electron spin resonance spectra of Ca-Fe-exchanged montmorillonite. Clays Clay Min. **34**, 645-650.
3. Banin, A., Carle, G.C., Cheng, S., Coyne, L.M., Orenberg, J.B. and Scattergood, T.W., 1988. Laboratory investigations of Mars: Chemical and spectroscopic characteristics of a suite of clays as Mars soil analogs. Origins of Life **18**, 239-265.
4. Banin, A., 1989. Mars soil - a sterile regolith or a medium for plant growth. "Case for Mars III". C. Stoker, ed., Science and Technology Series, American Astronautical Society. Volume 74, pp. 559-571.
5. Coyne, L.M., Bishop, J.L., Scattergood, T., Banin, A., Carle, G. and Orenberg, J., 1989. Near-infrared correlation spectroscopy. Quantifying iron and surface water in a series of variably cation-exchanged montmorillonite clays. Spectroscopic Characterization of Minerals and their Surfaces. ACS Symposium Series No. 415, L.M. Coyne, S.W.S. McKeever and D.F. Blake, editors, pp. 407-429.
6. Banin, A., Clark, B.C. and Wanke, H., Mars - Surface chemistry and mineralogy. Invited Review, The Mars Book, Univ. of Arizona Press, in press.

### Extended Abstracts of Presentations in Workshops

1. Coyne, L.M., Banin, A., Orenberg, J.B., Carle, G.C., Chang, S. and Scattergood, T.W., 1987. Chemical and spectroscopic characterization of a suite of Mars soils analogs. Nature and Composition of Surface Units on Mars. Workshop, Napa, CA. (Lunar and Planetary Institute and MEVTV Study Project), pp. 28-30.
2. Banin, A., 1988a. The soils of Mars. Mars Sample Return Science Workshop LIP Technical Report 88-07 (Lunar and Planetary Institute, Houston), pp. 11-12.
3. Banin, A., 1988b. The mineral components of dust on Mars. Workshop on Dust on Mars III (Lunar and Planetary Institute, Houston), pp. 1-3.
4. Banin, A., Margulies, L., Ben-Shlomo, T., Carle, G.C., Coyne, L.M., Orenberg, J.B. and Scattergood, T.W., 1988. Constraining Mars soil mineralogical composition: Palagonite vs. iron enriched smectite clays. Lunar Planet. Sci. Conf., 19th (Lunar and Planetary Institute, Houston), pp. 27-28.
5. Coyne, L.M., Banin, A., Carle, G.C., Orenberg, J.B. and Scattergood, T.W., 1988. Use of near-infrared correlation spectroscopy for quantification of surface iron, adsorbed water and stored electronic energy in a suite of Mars soil analog materials. ACS Annual Meeting, Los Angeles, 1988.
6. Banin, A. and Clark, B.C., 1989. Surface chemistry and mineralogy. 4th Intern. Conf. on Mars, Tucson, AZ, pp. 21-22.